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Influence of La on reduction behaviour and Ni metal surface area of Ni–Al₂O₃ catalysts for CO_x free H₂ by catalytic decomposition of methane

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ABSTRACT

A series of Ni:Al:La mixed oxides derived from hydrotalcite precursors with varying La/Al mole ratio were examined for CO_x free H₂ production by catalytic decomposition of CH₄. The physico-chemical characteristics of Ni:Al:La were determined by XRD, UV-DRS, SEM, TEM, Raman spectroscopy, BET-surface area, TPR and O₂ pulse chemisorption measurements. Addition of La to Ni–Al improved the Ni metal surface area and the reduction behaviour of NiO particles is dramatically changed. Particle size of Ni was similar to the size of carbon nano fibre in the deactivated catalyst. A direct correlation between Ni metal surface area and the CH₄ decomposition activity was observed.

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Introduction

Hydrogen has been identified as the fuel of the future because it has no environmental issues due to absence of harmful gases such as SO_x, CO_x and NO_x formation [1–3]. Due to negligible natural abundance of hydrogen, conventionally hydrogen is produced via catalytic steam reforming, partial oxidation and auto thermal reforming of natural gas or steam reforming of alcohols [4]. However, a major drawback with these routes is the formation of large amounts of CO_x as by-

products. Hydrogen generated by these methods can be utilized in fuel cells only if CO is completely eliminated. Since its presence even 10 ppm level in H₂ stream strongly deteriorates the efficiency of fuel cell anodic catalyst [5,6]. Therefore, catalytic decomposition of methane (CDM) has become a promising approach that produces clean H₂ with potentially useful carbon in the form of nano tubes and nano fibres without CO_x contamination [7–11]. Thus, produced hydrogen by CDM process is CO_x free that can be directly utilized not only in PEMFC without further purification also for various applications [5]. The second product is a graphitic carbon which has

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Table 1 – Physicochemical characteristics of Ni:Al:La catalysts with constant Ni and varied Al:La mole ratios.

Composition of Ni:Al:La		Surface area (m ² /g)	NiO domain size (nm)	H ₂ uptake (mmol/g _{cat}) TPR	O ₂ uptake (mmol/g _{cat})	S _{Ni} (m ² /g _{cat})	H ₂ yield (mols H ₂ /mol Ni)
Nominal	EDX						
(a) 2:1:0	2.06:0.94:0	120.0	8.3	9.6	3.2	17.0	1030
(b) 2:0.8:0.2	1.98:0.81:0.19	104.0	5.8	11.9	6.5	34.6	1550
(c) 2:0.7:0.3	1.97:0.72:0.308	93.9	5.3	13.6	7.2	38.5	1885
(d) 2:0.5:0.5	1.99:0.51:0.49	54.6	2.2	12.4	3.96	21.0	1478
(e) 2:0.1:0.9	1.98:0.09:0.92	30.3	2.0	11.5	0.8	4.3	370
(f) 2:0:1	2.08:0:0.92	20.3	7.3	10.2	0.45	2.6	108

many unique properties such as high resistant to strong acids, strong bases, as a H₂ storage material, in electronic switches, good mechanical strength and graphitic carbon with high surface area makes them useful materials as a catalyst support in thermo and photocatalytic process [9].

Transition metals such as Ni [7,12–14], Fe [15] and Co [16] are known active metals for methane decomposition. Particularly the nickel-based catalysts are active at low temperatures and provide higher yield of H₂ per unit mass of the active component [17–19]. However, these catalysts are easily deactivated at high temperatures. Hence, modification of Ni based catalysts opens up an interesting area to increase the H₂ yields and catalyst stability at higher temperatures in methane decomposition [20]. In this regard, introduction of second metal or metal oxides to a Ni catalyst provides significant changes in the activity and stability of the catalysts [21]. Doping of metals such as Cu, Rh, Pd, Ir and Pt to Ni catalysts were studied by Takenaka et al. and suggested that Pd doping alone increased the Ni activity through an alloying effect [20]. However, the other studies revealed that Cu doping significantly enhanced the performance of Ni catalysts towards methane decomposition for better H₂ yields [22–25].

In the past few years it is found that the rare earth oxides such as La₂O₃ can improve the catalytic properties of a variety of materials. Modification of Ni–Al by La₂O₃ is a topic of interest particularly in the steam reforming of alcohols at high reaction temperatures for the production of hydrogen [26]. The aim of this study is development of catalysts for the production of CO_x free hydrogen. In this investigation we have examined the influence of La on the nature and distribution of Ni–Al for CH₄ decomposition. The results indicated that the Ni particle size and its interaction with support played a major role on the hydrogen yields and longevity of the catalyst. Based on the obtained data, carbon growth mechanism is explained and the role of metal support interaction was discussed.

Experimental

Preparation of Ni–Al–La hydrotalcite precursors

The Ni:Al:La mixed oxides are obtained from their respective hydrotalcite (HT) precursors upon calcination in air at 550 °C/5 h. The Ni:Al:La HT precursors were prepared by a simple co-precipitation method. In a typical procedure, solution A containing a mixture of metal nitrates with constant Ni and

varied Al:La mole ratios; solution B containing a base mixture of 1:1 volume of 2M NaOH and 1M Na₂CO₃ were added slowly under vigorous stirring while maintaining a constant pH ~8.5 throughout the addition. Thus produced precipitate is thoroughly washed with distilled water until the pH reached to ~7 followed by drying at 100 °C for overnight and subsequently calcined in static air at 550 °C/5 h. The nominal and estimated compositions of the Ni:Al:La samples are reported in Table 1.

Characterization of catalysts

The experimental conditions for BET-surface area, powder X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscope-energy dispersive X-ray (SEM-EDX) and transmission electron microscopy (TEM) analyses were similar as reported by us earlier [14,18]. The XRD analysis of Ni:Al:La samples are carried out on a Rigaku Miniflex X-ray diffractometer using Ni filtered Cu K_α radiation ($\lambda = 0.15406$ nm) from $2\theta = 10$ – 80° at a scan rate of 2°min^{-1} . The specific surface areas of the calcined samples are calculated applying the BET method by N₂ adsorption at liquid N₂ temperature in an Autosorb 3000 physical adsorption apparatus. H₂-TPR and O₂-pulse chemisorptions were carried out in a quartz micro-reactor interfaced to a GC equipped with a thermal conductivity detector (TCD). The H₂ uptakes are measured by a calibration TPR profile of Ag₂O. Prior to O₂ pulse chemisorption, the sample (~0.10 g) reduced at 550 °C for 2 h in 5% H₂/Ar stream and flushed in helium at 550 °C/1 h, subsequently, the sample was cooled to 260 °C in helium, out gassed at this temperature for 30 min, followed by titration with 5.01% O₂ balance helium at 260 °C. The O₂ uptakes were calculated assuming the formation of surface NiO phase [27,28]. The carbon contents in deactivated samples were measured using a VARIO EL, CHNS analyser. The SEM-EDX of fresh and deactivated catalysts is recorded using a JEOL-JSM 5600 instrument. Transmission electron microscopy (TEM) is performed with a JEOL JEM 2010 transmission electron microscope. The UV–Vis spectra measured at room temperature using a UV-2000, Shimadzu Spectrophotometer equipped with a diffuse reflectance attachment with an integrating sphere containing BaSO₄ as a reference. The spectra were recorded in the range between 190 and 800 nm with sampling interval 0.5 nm and slit width 2 nm and the spectra were converted to Kubelka–Munk function. The Raman spectra for the structural characterization of deposited carbon in deactivated catalysts have been acquired with a Horiba Jobin-Yvon lab ram HR spectrometer using a laser beam excitation of $\lambda = 632.81$ nm.

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